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The Vapour Pressure of 20° K Equilibrium Hydrogen

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THE present work is part of a programme for the determination of the volumetric, thermodynamic, and transfer properties of 20° K equilibrium hydrogen, hereafter referred to simply as *para*-hydrogen. Most vapour pressures previously reported are limited to the region below approximately 1 atm.[2,3] White, Friedman, and Johnston[4] and Grilly[5] have reported measurements on normal hydrogen up to the critical point and to 3 atm, respectively. Hoge and Arnold[6] have published precise data on *para*-hydrogen up to the critical point. Hoge and Lassiter[7] have reported values of the critical constants. Comparison of the results of references 6 and 7 with *P–V–T* data obtained in this laboratory reveals small deviations which are generally within the claimed accuracies of the two measurements. The purpose of this report is to present this comparison of our vapour pressure determinations with those of Hoge and Arnold and a smooth representation of our data, useful for computation of densities[1] and thermodynamic functions. Results of the present investigation have been used in a forthcoming report on saturation properties of *para*-hydrogen.

Experimental

The apparatus used for the measurements was the *P–V–T* cryostat described by Goodwin.[8] Repeated determinations of the vapour pressure between 30 and 32·9° K provide an excellent test of the precision of the temperature and pressure measuring devices. Temperature was measured and controlled with a 25 Ω platinum resistance thermometer calibrated by the N.B.S. Temperature Physics section on the NBS-1955 scale. Errors in temperature control are considered negligible. Resolution of the dead weight gauge, fitted with the large piston, was about 0·0006 atm.

Samples used were taken from electrolytic hydrogen stored in clean steel cylinders. Mass spectral analysis showed that these cylinders contained less than 5 p.p.m. helium. *para*-Hydrogen analysis was accomplished with a thermal conductivity analyser.[9] Analysis depended upon comparison with normal hydrogen. Gas was passed slowly through the iron oxide catalyst until the analyser registered a constant maximum deflection. During the loading operation, gas was bled to the analyser from the filling stream to ensure that the composition remained constant. Composition was independent of the flow rate over the catalyst at the rates used.

A total of eleven different samples were used. Precision of the results confirms the uniformity of composition of the hydrogen.

Results

In the present study 38 datum points were obtained along the vapour pressure curve between the boiling point and the critical point. The normal boiling point is taken as 20·268° K in agreement with the adjusted value of Hoge and Arnold,[6] and this value was treated as a quasi datum point of double weight. The point at 33·0° K is actually above the critical temperature. It is on the critical isochore and was included to ensure good behaviour of the derivatives at the critical point. Between the boiling point and 29° K the data were smoothed, by means of a least-squares technique, with a function of the Antoine type,

$$\log_{10} P_a(\text{atm}) = A + \frac{B}{T+C} + DT \qquad \ldots(1)$$

Values of the constants are given in Table 1. Above 29° K the smooth curve falls below the data and an adjustment function must be used:

$$P = P_a + E(T-29)^3 + F(T-29)^5 + G(T-29)^7 \qquad \ldots(1a)$$

Values of the constants are given in the lower part of Table 1.

Table 1. Constants of Equations (1) and (1*a*)

A	2·000620
B	$-5{\cdot}009708 \times 10$
C	1·0044
D	$1{\cdot}748495 \times 10^{-2}$
E	$1{\cdot}317 \times 10^{-3}$
F	$-5{\cdot}926 \times 10^{-5}$
G	$3{\cdot}913 \times 10^{-6}$

The results of the fit are found in Table 2, wherein column 1 gives the temperature in degrees Kelvin on the

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NBS-1955 scale. The next three columns show the quality of the fit, in atmospheres. Column 4 shows that all experimental points except one agree with the smoothing function to within 0·002 atm, and most points agree within 0·001 atm. Columns 5 and 6 give the first and second derivatives of pressure with respect to temperature. The last column is for identification. The first two digits refer to an experimental run and the second two refer to the individual observation. The lower portion of Table 2 contains interpolated values in the region of the critical point. Table 2 can be interpolated, using tabulated first and second derivatives, with an error of less than 0·0004 atm.

Table 2

T (°K)	P (exp.) (atm)	P (calc.) (atm)	ΔP (atm)	1st der. (atm/deg.)	2nd der. (atm/deg^2)	Ident.
20·268	1·0000	0·9999	0·0001	0·2952	0.0632	
21·000		1·2334		0·3435	0·0690	
22·000	1·6124	1·6127	−0·0003	0·4165	0·0770	9401
23·000	2·0688	2·0691	−0·0003	0·4975	0·0851	9301
24·000		2·6105		0·5867	0·0934	
25·000	3·2462	3·2453	0·0009	0·6843	0·1017	9201
26·000	3·9826	3·9818	0·0008	0·7902	0·1102	9101
27·000	4·8285	4·8285	0·0000	0·9046	0·1188	9001
28·000	5·7920	5·7939	−0·0019	1·0277	0·1275	8901
29·000	6·8863	6·8869	−0·0006	1·1597	0·1365	8801
30·000	8·1162	8·1176	−0·0014	1·3044	0·1525	9501
30·000	8·1169	8·1176	−0·0007	1·3044	0·1525	9601
30·000	8·1171	8·1176	−0·0005	1·3044	0·1525	9701
30·500	8·7873	8·7892	−0·0019	1·3824	0·1594	9502
30·500	8·7885	8·7892	−0·0007	1·3824	0·1594	9602
30·500	8·7886	8·7892	−0·0006	1·3824	0·1594	9702
31·000	9·5023	9·5006	0·0017	1·4639	0·1666	8701
31·000	9·5029	9·5006	0·0023	1·4639	0·1666	9503
31·000	9·5005	9·5006	−0·0001	1·4639	0·1666	9603
31·000	9·5003	9·5006	−0·0003	1·4639	0·1666	9703
31·500	10·2525	10·2537	−0·0012	1·5496	0·1771	9504
31·500	10·2535	10·2537	−0·0002	1·5496	0·1771	9604
31·500	10·2539	10·2537	0·0002	1·5496	0·1771	9704
32·000	11·0502	11·0513	−0·0011	1·6424	0·1964	9505
32·000	11·0516	11·0513	0·0003	1·6424	0·1964	9605
32·000	11·0522	11·0513	0·0009	1·6424	0·1964	9705
32·500	11·8988	11·8984	0·0004	1·7488	0·2328	9506
32·500	11·8976	11·8984	−0·0008	1·7488	0·2328	9606
32·500	11·8989	11·8984	0·0005	1·7488	0·2328	9706
32·600	12·0749	12·0745	0·0004	1·7726	0·2432	9507
32·600	12·0742	12·0745	−0·0003	1·7726	0·2432	9607
32·600	12·0751	12·0745	0·0006	1·7726	0·2432	9707
32·700	12·2526	12·2529	−0·0003	1·7975	0·2549	9508
32·700	12·2520	12·2529	−0·0009	1·7975	0·2549	9608
32·700	12·2536	12·2529	0·0007	1·7975	0·2549	9708
32·800	12·4326	12·4340	−0·0014	1·8236	0·2679	9509
32·800	12·4330	12·4340	−0·0010	1·8236	0·2679	9609
32·800	12·4352	12·4340	0·0012	1·8236	0·2679	9709
32·900	12·6168	12·6177	−0·0009	1·8511	0·2825	9510
32·900	12·6187	12·6177	0·0010	1·8511	0·2825	9610
32·900	12·6183	12·6177	0·0006	1·8511	0·2825	9710
33·000†	12·8043	12·8043	0·0000	1·8802	0·2988	
32·955		12·7200		1·8669	0·2912	
32·960		12·7293		1·8684	0·2920	
32·965		12·7386		1·8698	0·2929	
32·970		12·7480		1·8713	0·2937	
32·975		12·7574		1·8727	0·2945	
32·980		12·7667		1·8742	0·2954	
32·985		12·7761		1·8757	0·2962	
32·990		12·7855		1·8772	0·2971	
32·995		12·7949		1·8787	0·2979	

† Point above the critical temperature included to ensure good behaviour of the derivatives at the critical point.

Comparison with previous results

For comparison of our data with those of Hoge and Arnold, it was necessary to adjust the latter to the NBS-1955 temperature scale. This was accomplished with the relationship

$$T(\text{Hoge and Arnold}) - 0{\cdot}01\,°\text{K} = T(\text{NBS-1955})$$

Figure 1 shows the difference between the resulting adjusted smooth table, from reference 6, and equation (1).

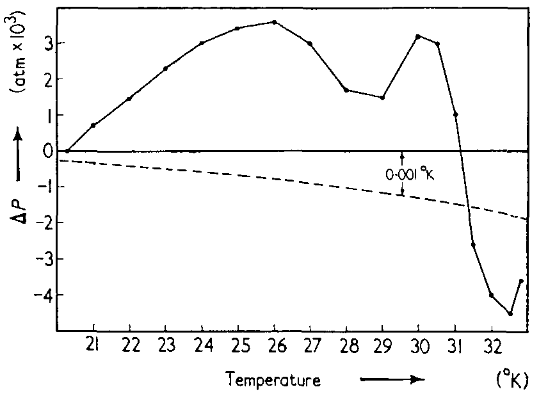

Figure 1. Deviations of adjusted vapour pressures of Hoge and Arnold from those calculated by equations (1) and (1a)

The dashed line illustrates the effect of a 0·001 degree error in temperature. The stated uncertainty of Hoge and Arnold varied from ±0·3 mm Hg (0·0004 atm) at the boiling point to ±8 mm Hg (0·0105 atm) near the critical point. The overall uncertainty of our pressure measuring system is believed to be ±0·003 atm at these pressures. It is obvious that there is a systematic deviation between the two curves although they agree within the combined uncertainties. This situation could be due to differences in the calibration of the thermometers although it seems unlikely that the rapid fluctuations between 30 and 33° K could be attributed entirely to this source. Incomplete conversion to *para*-hydrogen does not seem to be the reason, in view of the relatively good agreement between the different samples used.

Pressures below the boiling point

Our representation joins smoothly with the curve of

Hoge and Arnold in the region of the boiling point. A function of the form

$$\log_{10}P(\text{atm}) = a+\frac{b}{T}+cT \qquad \ldots(2)$$

fits the data of Hoge and Arnold within experimental deviations from the triple point to about 21° K. The constants are given in Table 3. Equations (1) and (2) join smoothly at 20·268° K, their first and second derivatives agreeing to within 0·3 per cent.

Table 3. Constants for Equation (2)

a	1·772454
b	$-4{\cdot}436888\times 10$
c	$2{\cdot}055468\times 10^{-2}$

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